

**QUANTUM YIELD OF THE FLUORESCENCE
OF DIACETYL**

BY

PHILIP ROGER GILLETTE

A.B., Cornell College, 1937

B.S., University of Illinois, 1938

M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS

**SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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QUANTUM YIELD OF THE FLUORESCENCE OF DIACETYL

In this investigation the quantum yield of the fluorescence of diacetyl vapor was measured as a function of exciting wavelength, pressure, and temperature. The fluorescence was excited by the mercury lines of wavelengths 4358 Å., 4047 Å., and 3650 Å., separated by a quartz monochromator, emitted by a 100 watt medium high pressure mercury lamp. The intensity of incident radiation and the absorption coefficient were measured with a photovoltaic cell. The fluorescence emitted in a small accurately measured solid angle was measured with vacuum photoemissive cells, in an electrometer tube circuit. Two thermopiles were used in the calibration of photoelectric cells. Evidence was obtained indicating that the response of blackened thermopiles depends upon the method of blackening and is not independent of wavelength in the region studied.

At 4358 Å. and 4047 Å., it was found that the yield always decreased slightly as the pressure was increased, and that the amount of decrease depended on the amount of radiation the sample had received. Plots of the reciprocal of the yield against pressure give straight lines which always intersect the $p=0$ axis at approximately the same point, irrespective of previous radiation treatment of the sample. We thus obtain an extrapolated yield of about 0.145 ± 0.035 for both exciting wavelengths. The dependence of the yield on pressure and previous radiation can be explained by assuming the presence of some quenching impurity which is consumed during radiation. At 3650 Å., the yield was found to rise from zero at zero pressure to a maximum, at a pressure of 5.0 cm. Hg, of 84% of the yield at the other two wavelengths obtained under similar conditions; this pressure effect is in approximate agreement with the results of Henriques and Noyes.¹

The quantum yield for 4358 Å. excitation decreases, as the temperature increases, nearly linearly in the range from

30°C. to 65°C.; the departures from a straight line, however, are such that the data may be fitted as well by a decreasing exponential function. The yield, after strong preradiation, at 65°C. was found to be 65% of the yield at 30°C.

The model proposed for diacetyl by Almy and Anderson² has been modified to account for the pressure effect at 3650 Å. The principal modification is in the assumption that absorption of 3650 Å. light excites a molecule to a vibrational level of the excited electronic state which is high enough to permit direct dissociation, unless collisions occur which remove vibrational energy and reduce the energy content of the molecule to an amount similar to that possessed by molecules excited by 4358 Å. light. New values for the transition rates and excitation energies involved in the model have been calculated on the basis of new data on the quantum yield, obtained in the present work, and the new value for the lifetime of diacetyl fluorescence obtained by Rawcliffe.³

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VITA

Philip Roger Gillette was born in Mt. Vernon, Iowa, on May 12, 1917. He attended the public schools of Calumet City, Illinois, graduating from high school in 1933. He attended Cornell College, Mt. Vernon, Iowa, from 1933 to 1936, and in 1936 he entered the University of Illinois. He was a Graduate Scholar in 1938-39, a Graduate Fellow in 1939-40, and from 1940 to 1942 he has been a part-time assistant in Physics. He received the degree of Bachelor of Arts from Cornell College in 1937, the degree of Bachelor of Science in Engineering Physics from the University of Illinois in 1938, and the degree of Master of Science from the University of Illinois in 1939.



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